Optical Properties of CdMnTe Film: Experimental and Theoretical Aspects

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CdTe thin films are representatives of $A^{II}B^{VI}$ crystal group and show semiconductor behavior. They are an important research field because of their wide applications in various fields of optoelectronic devices. A better opportunity to manage in a wide energy range the band gap E_g for practical applications exists with varying the content of CdTe-MnTe (from $E_g = 1.46$ eV for CdTe to $E_g = 3.1$ eV for MnTe). The titled compounds may be considered as a particular class of binary semiconducting compounds possessing promising optical parameters. $Cd_{1-x}Mn_xTe$ films were prepared on mica substrates by closed-space sublimation of polycrystalline $Cd_{0.88}Mn_{0.12}Te$ powders. X-ray diffraction studies revealed that the as-deposited films had a zinc blende structure with a preferential (111), (222) (333) and (444) orientations. Included Mn components cause the increase in the lattice parameters (compared with parent compound CdTe/mica). From EDS analysis it was observed that composition of the film was $Cd_{0.96}Mn_{0.04}Te$. The lattice parameter was refined by X-ray diffraction: $a = 0.6485(3)$ nm and $V = 0.2727(3)$ nm³. Results of study of transmission and reflection spectra of the $Cd_{0.96}Mn_{0.04}Te$ films-substrate combinations are present. The transmission and reflection spectra of the films exhibit periodic oscillations associated with the substrate. The spectral dependence of the optical absorption of $Cd_{0.96}Mn_{0.04}Te$ films in the $(\alpha h\nu)^2 - h\nu$ coordinates demonstrates the presence of the fundamental absorption edge. The value of the optical band gap of the $Cd_{0.96}Mn_{0.04}Te$ films was found to be equal to 1.465 eV and formed by direct interband optical transitions. Within the framework of the pseudopotential method, the dynamics of changing the parameters of the electronic subsystem of the $Cd_{1-x}Mn_xTe$ is theoretically studied. Using the Kramers-Kronig relations, the dielectric permeability, reflective index and reflectivity spectra that satisfactorily correlate with the experimental data are obtained.

Keywords: Quasi-close space sublimation, Thin films, Band gap, Transmission, Optical function.

1. INTRODUCTION

In recent years, $Cd_{1-x}Mn_xTe$ is believed to be a potential material for radiation detectors [1-3]. The primary interest of research has been focused on nuclear detectors fabricated by $Cd_{1-x}Mn_xTe$ single crystals [4].

To prepare $Cd_{1-x}Mn_xTe$ films different methods are used including electron deposition [5, 6], thermal evaporation [7], magnetron sputtering [8] and close-spaced sublimation (CSS) [9]. Thermal evaporation under vacuum by using CSS method is one of the most advantageous methods for obtaining uniform films [10, 11]. Our last work was focused at obtaining and optical-electronic study of $Cd_{1-x}Mn_xTe$ single crystals [12]. We take into account that for fabrication of large area radiation detectors based on $Cd_{1-x}Mn_xTe$ it is necessary to apply thick film technologies. We are continuing work connected with obtaining and optical studies of $Cd_{1-x}Mn_xTe$ films.

The aim of the present work is to investigate the structural and optical properties of $Cd_{1-x}Mn_xTe$ films which are produced on mica substrate by quasi CSS method. In this paper, we present results of theoretical and experimental investigation of the transmission and reflection spectra, refractive index and dielectric permeability.

2. EXPERIMENTAL

$Cd_{1-x}Mn_xTe$ films were obtained by quasi CSS method [13] at a pressure of $1 \cdot 10^{-6}$ Torr. Deposition of $Cd_{1-x}Mn_xTe$ films was conducted on mica substrate from polycrystalline $Cd_{0.88}Mn_{0.12}Te$ powder. The source and substrate material temperatures were 900 K and 700 K, respectively. The temperature was controlled using the PID-regulator of temperature PE-202 using a thermocouple of the type "K". The substrates of 14 mm in diameter were used for deposition of $Cd_{1-x}Mn_xTe$ films. Before $Cd_{1-x}Mn_xTe$ film deposition, the substrate surface was cleaned by boiling in a high purity CCl_4 solution during 0.5 h.

The phase analysis and crystal structure refinement were examined with using X-ray diffraction data on a STOE STADI P diffractometer at room temperature with $CuK_{\alpha 1}$ radiation. Details of the method of structural analysis were given in Ref. [14].

The spectral dependence of the optical transmittance (AvaSpec-2048) of the obtained samples in the visible and near infrared regions is studied at room temperature [12].

The theoretical calculations were performed within the framework of the density functional theory (DFT). To calculate the optical functions (dielectric permeability, reflective index and reflectivity spectra), we used electron band energy structure which was published in Ref. [12]. Using Kramers-Kronig relations [15], the spectral dependence of the optical constants was calculated.

3. RESULTS AND DISCUSSION

We present the results of calculation of optical spectra using electron band-energy structure (see Ref. [12]). Optical properties of materials can be studied by investigation of complex dielectric function $\varepsilon(\omega)$. Its imaginary part $\varepsilon_2(\omega)$ can be calculated from the momentum matrix elements between the occupied and unoccupied wave-functions [16]:

$$\varepsilon_2\left(\hbar\omega\right) = \frac{2e^2\pi}{V\varepsilon_0} \sum_{K,v,c} \left|\left\langle \Psi_K^c \left|\hat{\boldsymbol{u}} \cdot \boldsymbol{r}\right| \Psi_K^v \right\rangle\right|^2 \delta\left(E_K^c - E_K^v - \hbar\omega\right)$$

where u is the polarization vector of incident photon; Ψ_k^c and Ψ_k^v are the conduction and valence band wave-functions in $\boldsymbol{k}$-space, $\boldsymbol{r}$ is the electron position operator.

The real part $\varepsilon_1(\omega)$ of the dielectric function can be evaluated from the imaginary part $\varepsilon_2(\omega)$ by the Kramers-Kronig relation:

$$\varepsilon_1\left(\hbar\omega\right) - 1 = \frac{2}{\pi} \int_0^\infty \frac{t\varepsilon_2(t)dt}{t^2 - \left(\hbar\omega\right)^2}$$

From the spectrum of real and imaginary parts of dielectric function, refractive indices $n(\omega)$ and reflective spectra $R(\omega)$ can be obtained using the relations [17], respectively:

$$n = \sqrt{\frac{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} + \varepsilon_1}{2}}, \; R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} .$$

Calculated frequency dependences of the dielectric permeability, reflective index and reflection spectra for $Cd_{0.875}Mn_{0.125}Te$ solid solution are presented in Fig. 1-Fig. 3, respectively. Obtained theoretical optical spectra show the first peak, which corresponds to the absorption edge. To compare theoretical and experimental results, we synthesized $Cd_{1-x}Mn_xTe$ $(x = 0.12)$ film. The results of experimental studies are shown below.
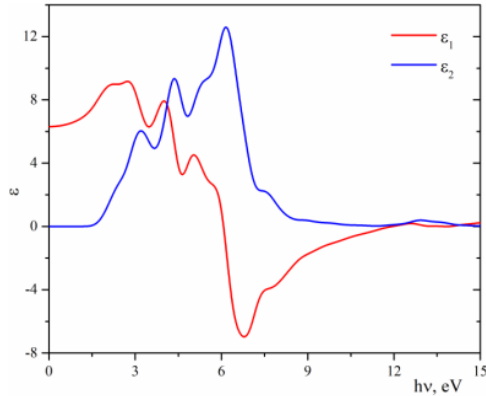

Fig. 1 – Real (ε_1) and imaginary (ε_2) parts of the dielectric permeability spectra for $Cd_{0.875}Mn_{0.125}Te$ solid solution for unpolarization light (GGA)
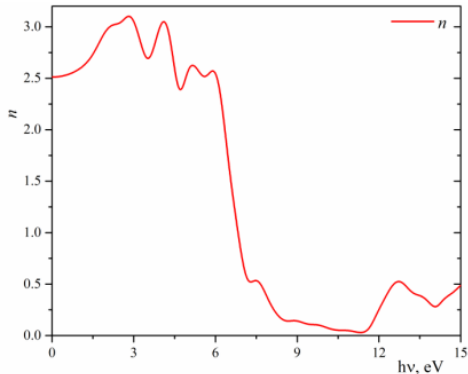

Fig. 2 – Refractive index for $Cd_{0.875}Mn_{0.125}Te$ solid solution for unpolarization light (GGA)

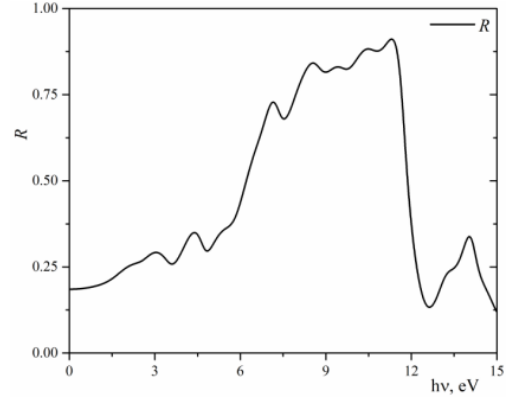**Fig. 3** – Reflectivity spectrum for $Cd_{0.875}Mn_{0.125}Te$ solid solution for unpolarization light (GGA)

EDS analysis was used to evaluate the composition and purity of $Cd_{1-x}Mn_xTe$ films. The composition of the film was $Cd_{0.96}Mn_{0.04}Te$. Mn content in this polycrystal-line film was much lower than that found in the source (see experimental details). The same situation was realized in work [18]. This composition change is also observed when depositing $Cd_{1-x}Zn_xTe$ films and is caused by the nonequilibrium deposition of the CSS growth process [19].

From the analysis of the X-ray diffractogram of $Cd_{0.96}Mn_{0.04}Te$ (CdMnTe) (Fig. 4) it is seen that the film is comprised of a single phase with small impurity phases. The compound CdMnTe belongs to the $F43m$ symmetry point group (ZnS structure type). A corrected unit cell parameter is given in Table 1. A detailed analysis of the positions of experimental reflexes and their intensities compared to the theoretical peaks showed very strong preferred orientation of grains of the CdMnTe phase in the synthesized film (texture). Reflexes from planes with (111), (222), (333) and (444) hkl Miller indices are observed, whereas reflexes with other sets of hkl are almost completely quenched in intensity (the same situation is realized in CdTe [13]). Insignificant noise that is present can be explained by the contribution of the substrate.

Included Mn components cause the increase in the lattice parameters (compared with parent compound CdTe/mica (see Table 1)). It can be assumed that a CdTe film doped with Mn atoms forms. For the result-ing CdMnTe solid solution, the lattice parameters should decrease with increasing Mn concentration. But the same situation is realized in another solid solution [14]. Based on the results for other compounds [13, 14], we assumed that a solid solution was formed.

The impurity phases do not correspond to binary compounds (CdTe or/and MnTe). We suggest that im-purity phases related to the reaction of manganese with mica substrate are observed.

Fig. 5 shows the transmission spectrum of the CdMnTe film-substrate combinations. The transmis-sion coefficient strongly depends on the film structure, which is determined by the preparation methods, film thickness and deposition conditions. The transmission and reflection (Fig. 5, Fig. 6) spectra of the films exhibit periodic oscillations associated with the substrate. Peaks obtained at 520 and 700 nm from the reflectance spectra may be related to substrate defects.
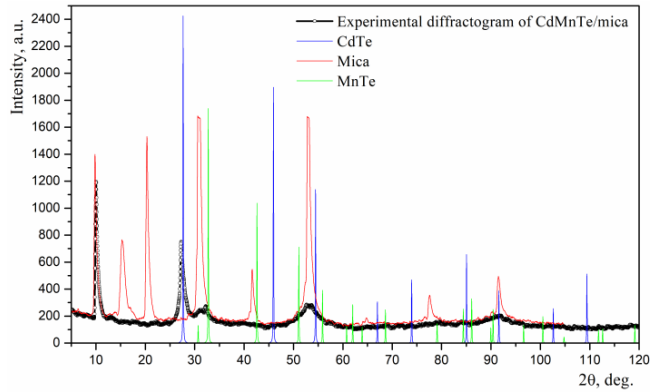
Fig. 4 – Measured and calculated XRD patterns for CdMnTe (CuKα₁ radiation). Experimental data (circles) and calculated profile (solid line) indicated in the legend

Table 1 – Structural data for CdMnTe solid solution (ZnS structure type)

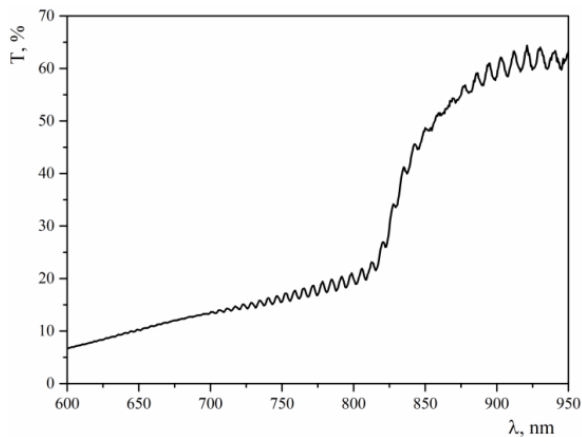| Sample	Space group	a, nm	V, nm³
$Cd_{0.96}Mn_{0.04}Te/mica$	$F43m$	0.6485(3)	0.2727(3)
CdTe/mica [13]	$F43m$	0.64765(19)	0.2717(2)
$Cd_{0.968}Mn_{0.032}Te$ [12]	$F43m$	0.64647	0.27018

Fig. 5 – Transmission spectra of CdMnTe film at room temperature

The spectral dependence of the optical absorption of CdMnTe films in the $(\alpha h\nu)^2 - h\nu$ coordinates (see Fig. 7) demonstrates the presence of the fundamental absorption edge. Extrapolation of linear segments of the $(\alpha h\nu)^2$

Fig. 6 – Reflection spectra of CdMnTe film at room temperature

Fig. 7 – Spectral dependence of optical absorption for CdMnTe film

curve until intersection with the axis of energies (see Fig. 8) was carried out by the techniques described in [20], and the value of the optical band gap of CdMnTe films was found to be equal to 1.465 eV (Table 2).

The linear behavior of $(\alpha h\nu)^2 = f(h\nu)$ dependences in the range of 1.46-1.55 eV indicates the formation of the absorption edge by direct interband optical transitions.

The observed discrepancy with the experimental data is insignificant. Thus, we can affirm that the chosen calculation technique can be successfully applied to predict the optical and energy properties of films.

Table 2 – Optical parameters of $Cd_{1-x}Mn_xTe$ film obtained from experimental ($x = 0.04$) and theoretical ($x = 0.125$) studies

Parameters	Direct band gap, eV				$\lambda = 700$ nm		
					R, %	R, %	n
Reference	This work (experimental)	This work (calculation)	CdMnTe ($x = 0.032$) [12]	This work ($x = 0.04$; calculation using equation from [12])	This work (experimental)	This work (calculation)	This work (calculation)
Value	1.465	1.48	1.496	1.5432	~ 22	~ 24	~ 2.95

4. CONCLUSIONS

This work was focused on basic research of optical parameters of $Cd_{1-x}Mn_xTe$ film. $Cd_{1-x}Mn_xTe$ film was obtained by quasi CSS deposition method on mica substrate from polycrystalline $Cd_{0.88}Mn_{0.12}Te$ powder. We observed that Mn content in this polycrystalline film was much lower than that found in the source. It was revealed from
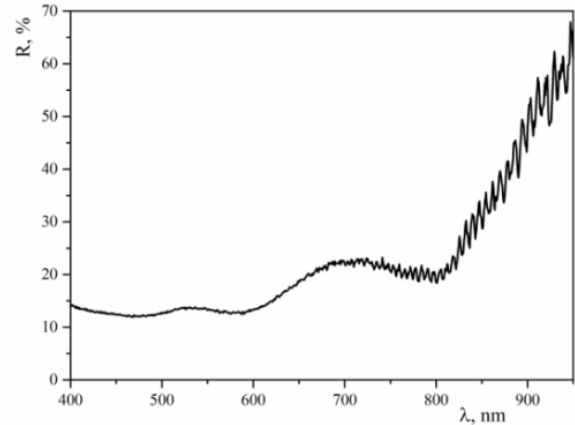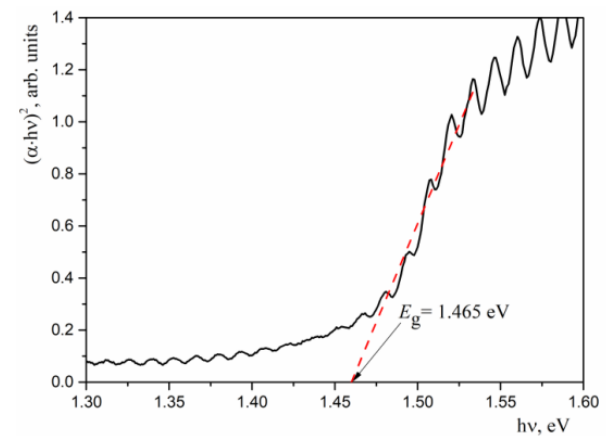
EDX analysis that composition of the film was $Cd_{0.96}Mn_{0.04}Te$. X-ray diffractogram of $Cd_{0.96}Mn_{0.04}Te$ film showed that the film is comprised of a single phase with small impurity phases. Compound $Cd_{0.96}Mn_{0.04}Te$ belongs to the $F43m$ symmetry point group (ZnS structure type).

The transmission and reflection spectra are discussed. The optical band gap of CdMnTe films was found to be equal to 1.465 eV.

The theoretical calculations were performed within the framework of the DFT. It was found that the optical spectra calculated *ab initio* agreed rather well with the experimental data.

The possibility of using other substrates for deposition of $Cd_{1-x}Mn_xTe$ films and research of electrical properties (testing as materials for nuclear sensor) should serve as the basis for further studies.

REFERENCES

1. H. Ji, J. Huang, L. Wang, J. Wang, J. Lai, R. Xu, J. Zhang, Y. Shen, J. Min, L. Wang, Y. Lu, *Appl. Surf. Sci.* S0169433215029645 (2015).
2. A. Burger, K. Chattopadhyay, H. Chen, J.O. Ndap, X. Ma, S. Trivedi, S.W. Kutcher, R. Chen, R.D. Rosemeier, *J. Crystal Growth* **198-199**, 872 (1999).
3. D. Zeng, W. Jie, H. Zhou, Y. Yang, *Thin Solid Films* **519**, 4158 (2011).
4. L.A Najam, N.Y. Jamil, R.M. Yousif, *Ind. J. Phys.* **86**, 267 (2013).
5. A. Bansal, P. Rajaram, *Mater. Lett.* **59**, 3666 (2005).
6. N.B. Chaure, S. Chaure, R.K. Pandey, *Electrochim. Acta* **54**, 296 (2008).
7. G. Zha, H. Zhou, J. Gao, T. Wang, W. Jie, *Vacuum* **86**, 242 (2011).
8. P. Banerjee, R. Ganguly, B. Ghosh, *Appl. Surf. Sci.* **256**, 213 (2009).
9. X. Wu, *Sol. Ener.* **77**, 803 (2004).
10. V.V. Brus, L.J. Pidkamin, S.L. Abashin, Z.D. Kovalyuk, P.D. Maryanchuk, O.M. Chugai, *Optical Mater.* **34**, 1940 (2012).
11. V.V. Brus, M.N. Solovan, E.V. Maistruk, I.P. Kozyarskii, P.D. Maryanchuk, K.S. Ulyanytsky, J. Rappich, *Phys. Solid State* **34**, 1947 (2014).
12. R.Yu. Petrus, H.A. Ilchuk, V.M. Sklyarchuk, A.I. Kashuba, I.V. Semkiv, E.O. Zmiiovska, *J. Nano- Electron. Phys.* **10**, 06042 (2018).
13. H.A. Ilchuk, R.Y. Petrus, A.I. Kashuba, I.V. Semkiv, E.O. Zmiiovska. *Nanosistemi, Nanomateriali, Nanotehnologii* **16**, 519 (2018).
14. A.I. Kashuba, M. Piasecki, O.V. Bovgyra, V.Yo. Stadnyk, P. Demchenko, A. Fedorchuk, A.V. Franiv, B. Andriyevsky, *Acta Phys. Pol. A,* **133**, 68 (2018).
15. M. Dressel, B. Gompf, D. Faltermeier, A.K. Tripathi, J. Pflaum, M. Schubert, *Opt. Express* **16**, 19770 (2008).
16. P.E. Van Camp, V.E. Van Doren, *Solid State Commun.* **91**, 607 (1994).
17. D.L. Greenway, G. Harbeke, *Optical properties and band structure of semiconductors* (New York: Pergamon Press: 1968).
18. J. Lai, J. Wang, L. Wang, H. Ji, R. Xu, J. Zhang, J. Huang, Y. Shen, J. Min, L. Wang, Y. Xia, *J. Vacuum Sci. Technol. A: Vacuum, Surf. Films* **33**, 05E125 (2015). DOI: 10.1116/1.4927820
19. V. Kosyak, A. Opanasyuk, P.M. Bukivskij, Yu.P. Gnatenko, *J. Cryst. Growth* **312**, 1726 (2010).
20. S. Bloom, T.K. Bergstresser, *Solid State Commun.* **6**, 465 (1968).

Оптичні властивості плівки CdMnTe: експериментальні та теоретичні аспекти

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Тонкі плівки CdTe є представниками кристалічної групи $A^{II}B^{VI}$ і демонструють поведінку напівпровідників. Вони є важливим напрямком досліджень через широке застосування в різних галузях оптоелектронних пристроїв. Краща можливість керувати в широкому енергетичному діапазоні, наприклад, шириною забороненої зони E_g для практичних застосувань існує при зміні вмісту CdTe-MnTe (від $E_g = 1.46$ еВ для CdTe до $E_g = 3.1$ еВ для MnTe). Названі сполуки можуть розглядатися як особливий клас бінарних напівпровідних сполук, що мають перспективні оптичні параметри. Плівки $Cd_{1-x}Mn_xTe$ було отримано методом квазізамкненого об'єму. Осадження плівок проводилось з полікристалічного порошку $Cd_{0.88}Mn_{0.12}Te$ на підкладку слюди. З аналізу дифрактограми для $Cd_{1-x}Mn_xTe$ встановлено, що плівка є однофазною. Фаза – сполука CdTe (структурний тип – ZnS, просторова група – $F43m$). Детальний аналіз положення експериментальних рефлексів та їхніх інтенсивностей у порівнянні із теоретичними засвідчив дуже сильну переважну орієнтацію зерен фази $Cd_{1-x}Mn_xTe$ у синтезованій плівці (текстуру). Спостерігаються рефлекси від площин з індексами Міллера hkl (xyz). Включення манганової компоненти є причиною збільшення параметрів ґратки (порівняно з вихідним з'єднанням CdTe/слюда). З аналізу EDS було встановлено, що композиційний склад плівки становить $Cd_{0.96}Mn_{0.04}Te$. Уточнений параметр елементарної комірки $a = 0.6485(3)$ нм і $V = 0.2727(3)$ нм³. Наводяться результати дослідження спектрів пропускання та відбиття структури $Cd_{0.96}Mn_{0.04}Te$/слюда. Спектри пропускання та відбиття плівки демонструють періодичні коливання, які викликані особливістю підкладки. Спектральна залежність оптичного поглинання плівок $Cd_{0.96}Mn_{0.04}Te$ у координатах $(\alpha h\nu)^2 - h\nu$ демонструє наявність основної грані поглинання. Найменше значення ширини забороненої зони для плівки $Cd_{0.96}Mn_{0.04}Te$ становить 1,465 еВ і характеризується прямим міжзонним оптичним переходом. В рамках методу псевдопотенціалу теоретично вивчається динаміка зміни параметрів електронної підсистеми $Cd_{1-x}Mn_xTe$. З використанням співвідношень Крамерса-Кроніга отримані діелектрична проникність, спектр відбиття та спектральна залежність показника заломлення. Теоретичні та експериментальні результати задовільно корелюють між собою.

Ключові слова: Метод квазізамкненого об'єму, Тонка плівка, Заборонена зона, Пропускання, Оптичні функції.